ON THE GENESIS OF NATURAL GAS AND PETROLEUM.

BY FRANCIS C. PHILLIPS.

(Read February 5, 1897.)

If it were possible to demonstrate that the original source of petroleum and natural gas is to be looked for in the rock strata in which they are now found to occur, an important advance could be made towards the establishment of a satisfactory hypothesis to account for the genesis of these hydrocarbons in nature.

It has often been supposed that the relationship of the hydrocarbons to the rocks in which they occur is of an intimate kind, and that the geological record should supply all the data upon which a conclusion as to the origin of gas and oil is to be based. It does not necessarily follow, however, that they are products of Devonian or Silurian time because of their association with certain sandstones, limestones or shales.

The presence of a gaseous or liquid hydrocarbon in a particular rock is perhaps due to the fact that the region of this rock, on account of its open texture, has been one of least resistance to the movement of a fluid under pressure. It is possible that gas and petroleum may have invaded the Devonian strata from greater depths and that their present position is wholly due to the pressure to which they have at some former period been subjected.

Other circumstances may have been factors in determining their present location. An abundance of subterranean water may have caused a transfer to a higher level. Differences of temperature might involve a partial fractionation or distillation and removal to distant regions. Hydrocarbons of different character and from different sources might become mingled and thus intrinsic signs of different modes of origin be obliterated. In view of these inherent difficulties, which impede a solution as viewed from the geological standpoint, the question seems to resolve itself for the present into a broader but less definite one which might be formulated thus: What are the chemical processes which, being logically assumed in connection with known facts of geology, could have produced from the compounds of carbon and hydrogen in the rocks the vast quantities of bitumen, petroleum and natural gas?

Of the hypotheses proposed many have been based upon phenomena which are more or less local when geologically considered, even if occurring in terranes of wide extent. One hypothesis attributes to petroleum and natural gas an origin almost cosmical.

This hypothesis, suggested by Berthelot and afterwards developed by Mendeléeff (*Principles of Chemistry*, Vol. i, p. 364), and restated by this author in 1889, supposes that metallic carbides have been produced deep in or below the earth's crust, and that these carbides have been decomposed by steam giving rise to the various hydrocarbons of oil and gas. Mendeléeff supposes that carbides of the heavier metals, and among these especially iron, have been mainly instrumental in the process. The correctness of this hypothesis, which depends upon so direct an appeal to chemical facts, must be tested by a consideration of the laws of chemistry in so far as they bear upon the question.

According to the experiments of Moissan (*Compts Rendus*, Vol. 122, p. 1462), a few only of the metals are capable of forming definite carbides, even at the temperature of the electric arc. These are chiefly the alkali, alkaline earth and earth metals. Aluminum and beryllium are the only metals whose carbides yield a hydrocarbon of the paraffin series alone (methane) on decomposition by water. The action of water upon the carbides of the metals of the alkalies and alkaline earths produces acetylenes. In the case of the carbides of some heavier metals methane is produced in admixture with free hydrogen and ethylene. The results of this author's experiments would seem to lead to the conclusion that the carbides of the earth metals only can be assumed to have participated in the process of petroleum and gas formation, in accordance with Mendeléeff's hypothesis, if the chemical composition of natural gas as found in western Pennsylvania is taken into consideration.

There are few elements known to chemistry whose relationships towards carbon at high temperatures are better known than iron. The action of steam upon iron in its pure state and when in combination with carbon is also sufficiently well understood to justify a criticism of the hypothesis upon chemical grounds. It is a fact of importance that the product of the action of superheated steam upon cast iron consists mainly of free hydrogen with small quantities of hydrocarbons, including olefins, paraffins and others of unsaturated character.

It may be assumed, but hypothetically, that iron exists in the rocks

in form of a carbide richer in carbon than is producible in the electric furnace, and therefore resembling the carbides of aluminum as regards its action upon water. In such case a gas somewhat similar to natural gas might result. Published analysis of meteoric iron and of iron found in plutonic rocks do not tend to show, however, that the iron found in nature ever contains carbon in such quantity as to lead to the belief that a definite carbide of this metal exists comparable to the carbides of aluminum, akaline earth, and alkali metals.

If aluminum carbide and the carbides of related metals are to be regarded as the source of natural gas, we must look for the occurrence of the lighter metals at depths at which the hypothesis of Mendeléeff would require us to suppose that the heavy metals predominate. It seems, therefore, probable that a few only of the metals in form of carbides could have been concerned in the production of natural gas, and these are the very metals which on account of their lightness are supposed by this hypothesis to give place to those of high specific gravity in regions where the chemical changes in question have occurred.

On account of its stronger affinity for oxygen, aluminum may be supposed under all conditions tending towards oxidation to assume the form of an oxide more readily than iron, and where aluminum occurs in presence of the heavier metals it will probably precede these in the order of time in uniting with oxygen. But its oxidation would remove it from the sphere of action leading to the production of hydrocarbons.

The conclusion seems justified that where aluminum occurs in a metallic state, or as a carbide, below or in the earth's crust, the heavy metals will also abound and notably iron.

If the chemical composition of natural gas is such as to warrant the belief that its production was due to the action of steam upon iron carbide, the hypothesis of Mendeléeff would at once receive strong support. If, on the other hand, chemical considerations show that iron cannot have been concerned in the process, the question then arises, Why has iron carbide been suppressed in the subterranean reactions giving origin to natural gas?

The term iron carbide has here been used to signify iron containing a little carbon, such as cast iron, but not implying a real compound containing iron and carbon in atomic proportions.

Analytical data concerning natural gas drawn from deep-lying

strata must prove of importance in the discussion of the subject. The hypothesis of Mendeléeff would suggest that if free hydrogen occurs among the hydrocarbons contained in any geological formation it must be looked for in those strata which are nearest above the Archæan rocks, and where protection against loss by diffusion upward is as nearly as possible assured by great thickness of compact overlying beds.

Believing the composition of natural gas from formations of considerable depth to be a matter of interest, some tests were made during August, 1896, of natural gas from a well drilled down through the Trenton limestone at Stevensville, county of Welland, Ontario, Canada. This well is twenty-nine hundred feet deep and stratified formations below its bottom are locally of slight depth, so that, according to Mr. E. Coste, the engineer for the gas company, the drill has in the case of this well penetrated to within a short distance only of the Archæan rocks. Shales sixteen hundred feet in thickness shut off possible communication between the Trenton limestone and the upper gas-producing rocks (the Medina sandstone, Clinton limestone and Niagara limestone), and there seemed every reason to suppose that the gas was derived exclusively from very deep-lying measures. The tests were made at the well, and thus the possibility of errors due to leakage during transportation of a sample were avoided. The method employed I have described in the *American Chemical Journal* for 1894, page 258.

Tests were also made at the well by methods which have been devised for such purposes, and which have been described in the same volume of the journal named, for acetylene and carbon monoxide. The results of all these trials were negative. Numerous tests have been made of gas from wells scattered over various parts of western Pennsylvania which seem to justify the conclusion that free hydrogen, acetylene and carbon monoxide are not found in the natural gas of the region.

The absence of free hydrogen in natural gas might be explained upon the assumption that although originally present, it has, by reason of its extreme lightness and ready diffusibility passed out through overlying rock strata and made its way to the upper regions of the atmosphere. In such case we must suppose that as a result of the production of free hydrogen in the interior of the earth, the atmosphere now contains in its more rarified portion a considerable and gradually increasing volume of this very light gas.

Mendeléeff's hypothesis implies that the production of natural gas still continues, there being no reason to suppose that the iron or other metallic carbides below the earth's surface are exhausted. Consequently much importance must be attached to the question of the presence of free hydrogen.

Accepting provisionally the hypothesis of Mendeléeff, it may be asserted that if natural gas is a contemporaneous product sufficient time has not yet elapsed for the escape by diffusion of the free hydrogen through some hundreds or thousands of feet of shales and limestones. The free hydrogen originally present should still occur in the gas of different regions and be recognizable by chemical tests. If, on the other hand, natural gas is a stored product, shut in for long ages, it might seem possible that comparatively impervious rock strata would not have sufficed to prevent the escape of this highly diffusible constituent in the course of time.

No hypothesis regarding the origin of natural gas can be accepted as satisfactory if it should require the assumption that the chemical changes involved in the process are such as to lead to the production of much free hydrogen, unless it can be positively demonstrated that free hydrogen occurs as a common constituent of the gas which flows from a drill hole.

The foregoing criticisms have been directed more particularly to the hypothesis in so far as it relates to natural gas. The author of the hypothesis has apparently avoided a distinction between natural gas and petroleum, and to the various hydrocarbons, liquid or gaseous, he assigns a common origin. It has been common to consider such compounds as closely related genetically. Yet this supposition may not have sufficient basis. Mabery (*American Chemical Journal*, 1896, p. 43) has shown that benzene and its homologues occur in some of the Ohio and Canadian petroleums. Lengfeld and O'Neill (*American Chemical Journal*, 1893, p. 19) have also discovered members of the same series of hydrocarbons in petroleum from southern California. Similar observations have been made by other authors.

The composition of natural gas is such as to suggest that it has been produced by reactions occurring at low temperature, and there is reason to suppose that it has not been exposed to temperatures exceeding 500° C., since the time of its formation, as experiments demonstrate that at temperatures ranging from this point up to that of melting gold, its constituents suffer more or less complete dissoci-

ation, yielding hydrogen and carbon together with small quantities of unsaturated hydrocarbons, notably acetylene. On the other hand, petroleum has been shown by the important researches of Mabery to contain a series of hydrocarbons which are usually characteristic of reactions at high temperatures. The fact that such hydrocarbons occur in petroleum, whether in small or large quantities, is of very great interest and should have due weight in the selection of any hypothesis proposed to account for its origin. At present this fact can hardly be considered to furnish evidence either for or against the views of Mendeléeff in regard to the origin of natural gas.

ON THE OCCURRENCE OF PETROLEUM IN THE CAVITIES OF FOSSILS.

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(Read February 5, 1897.)

In the study of geological facts bearing upon the history of petroleum, much interest has been aroused during recent times by the discovery of petroleum enclosures in the cavities of fossils in limestone rocks. Such occurrences, observed in many places, and in deposits of different geological age, from the Silurian onward, have been regarded as furnishing proof that the genesis of oil is to be attributed to chemical changes taking place in the tissues of the original organism of the fossil, and therefore as strengthening a commonly accepted belief that the hydrocarbons contained in the rocks have originated from animal remains stored in the sediments which afterwards became consolidated into rock.

The relationship suggested between the petroleum and the fossils is all the more interesting and important since the oil-bearing sand rocks of the Devonian age do not, as a rule, contain remains of animal life, and furnish no satisfactory clues as to the origin of oil and gas. As tending to confirm the evidence which such facts have been supposed to furnish, numerous instances have been cited where hydrocarbons are apparently produced from remains of more recent animal life, as in coral reefs and in the accumulations of organic remains buried under marine or fluviatile sediments. In certain